Nanocellulose Based Facilitated Transport Membranes for CO$_2$ Separation

Davide Venturi[a], Luca Ansaloni[b], Marco Giacinti Baschetti[a]*

[a]Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, University of Bologna, Italy
[b]Department of Chemical Engineering, Norwegian University of Science and Technology, Norway
marco.giacinti@unibo.it

In the present work the performance of a new membrane material, based on Microfibrillated Cellulose (MFC), was investigated in view of its use in CO$_2$ separation applications. In particular the membranes were obtained by casting, from a solution of carboxymethylated MFC and Lupamin (a Polyvinylamine produced by BASF), followed by a thermal treatment at 105 °C. Permeability of CO$_2$ and CH$_4$ were measured at 35 °C as a function of relative humidity and water sorption experiments were performed as well to relate the previous results to the actual water content in the membrane. As a reference, pure MFC films have been also prepared and their gas permeability tested in the same conditions. The overall results suggest that both MFC and MFC-Lupamin films have really interesting performance for the CO$_2$/CH$_4$ separation showing very high selectivity values (higher than 400) which place both materials well above the trade-off curve of 2008 Robeson's plot. In particular MFC films showed higher maximum selectivity but lower average CO$_2$ permeability with respect to the MFC-lupamin blends probably because of the different level of water absorbed by the two materials. Pure MFC indeed never exceeded 10% water uptake, while the Polyvinylamine blend showed water sorption very similar to the previous material up to 60% RH; it then definitely increased, reaching a mass uptake higher than 50% at the maximum water activity inspected.

1. Introduction

In recent years, the environmental concern regarding the accumulation in the atmosphere of greenhouse gases and CO$_2$ in particular, due to anthropogenic activities, has increased. Thus, capturing carbon dioxide before the emission in the atmosphere, as well as its subsequent storage, has become crucial to prevent its dispersion in the environment (Aaron and Tsouris, 2005). The separation of CO$_2$ from light gases such as N$_2$, CO, CH$_4$, and H2 is traditionally performed by means of reversible absorption methods using chemical and/or physical solvents. However, these kinds of techniques suffer from a variety of problems, ranging from the use of harmful organic solvents, difficult operability and low energy efficiency (Baker, 2002); cheaper and more energy efficient methods are thus needed to perform this separation. During the last years a higher interest has been shifted toward the use of gas separation membranes (Bernardo and Clarizia, 2013) as an efficient and more straightforward technology for CO$_2$ capture (Aaron and Tsouris, 2005). Amongst these, an interesting category is represented by facilitated transport membranes, in which the permeation of a specific molecule (in this case carbon dioxide) relies on a reversible reaction with functional groups embedded in the matrix membrane, named carriers (Noble, 1992). The first examples of these materials were developed by Ward and Robb (1967) and were based on supported liquid membranes (SLM) where CO$_2$ molecules could bond with functional group capable of permeating through the film and releasing them on the downstream side. However, despite the high performances, these membranes lacked severely in terms of long-term stability, because of carrier leakages. In order to tackle this problem, the research has been focused on Fixed Site Carrier (FSC) membranes, in which the functional groups are covalently bond to the polymeric backbone, hence drastically improving their stability. An attractive polymeric material to prepare FSC films is Polyvinylamine (PVAm) (Kim et al., 2004), due to the large amount of amine moieties present within the membrane matrix. In presence of water, these amine groups are able to interact with CO$_2$ according to the following reaction (Tong et al., 2015):

$$R - NH_2 + H_2O + CO_2 \leftrightarrow R - NH_3^+ + HCO_3^-$$
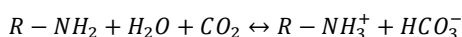
In addition, the amine groups can also play the role of catalyst in the CO_2 hydration reaction, as proposed by Deng and Hagg (2014):

$$H_2O + CO_2 \leftrightarrow H^+ + HCO_3^-$$
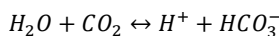
Despite the promising separation performance, PVAm can suffer from instability issues, due to the poor mechanical properties achieved at high humidity. However, this problem is usually overcome by blending PVAm with a "structural" polymer, which can increase the mechanical properties of the matrix under high humidity conditions, still allowing the facilitated transport mechanism. Typically, Polyvinylalcohol (PVA) is adopted for this purpose and in several works (Zou and Ho 2006; He et al. 2014) PVAm has been blended with PVA showing promising separation performance. The good compatibility between the two polymers is to be found in the high polarity and water affinity of both amine and hydroxyl groups.

The present work analyses the behavior of a film, which employs Microfibrillated cellulose (MFC) (Minelli et al. 2010), as a structural material in place of PVA, which has been successfully blended with PVAm to prepare self-standing polymeric films. Furthermore, the membranes have been subjected to a curing process at high temperature (105 °C) under vacuum conditions, in order to improve the stability of the membrane at high humidity, lowering the water uptake and limiting the matrix swelling, which is believed to induce strong losses in selectivity of the material. It is indeed known that amines and carboxylic groups can react at high temperature forming amide bonds (Jursic and Zdravkovski, 1993) while the decrease in the water sorption in cellulose fibers subjected to an intensive drying is a well-known phenomenon usually referred to as "hornification" (Weise, 1998). This seems to be related to fibers shrinkage (Minor, 1994) and cellulose co-crystallization (Idström et al. 2013), even though a complete and widely accepted explanation of the causes has not been obtained yet.

Carbon dioxide and methane permeability as well as water solubility were then measured in order to characterize the new membrane materials as a new possibly promising material for CO_2 separation.

2. Materials

Microfibrillated cellulose (MFC) used for membrane preparation performed in the present work was kindly provided by Professor Tom Lindström of Innventia AB (Stockholm, Sweden) under the name of MFC G2 (Generation 2). The cellulose has a hemicellulose and lignin content of respectively 4.5 % and 0.6 % and was subjected to carboxymethylation prior to the high pressure homogenization step. This lead to microfibrils with diameter in the range of 5-15 nm and surface charge density in the order of ~586 µequiv/g. The cellulose was received as a water suspension with a solid content of 2.17 % (Wågberg et al., 2008). Polyvinylamine has been kindly provided by BASF Italia S.p.A. (Cesano Maderno, Italy) as a water solution named Lupamin 9095 (95 % hydrolyzation grade) with a solid concentration in the range of 20-22 %wt. (the value of 21 %wt. has been assumed to calculate its content in the membranes). Both materials have been used without further purification.

3. Methods

3.1 Film preparation

For the preparation of <u>pure MFC films</u>, the MFC G2 suspension was used as received and poured in a Polystyrene petri dish of 8.5 cm in diameter; the water was then evaporated by leaving the suspension in a ventilated oven overnight at 40 °C. After that, the film was peeled off the dish and the final thickness was measured to be about 30 µm. On the other hand for the preparation of <u>MFC/PVAm blends</u>, the MFC suspension was mixed directly with PVAm solution, in order to reach a 50:50 weight ratio between the two solid contents. Overall, the final solid concentration was calculated to be approximately 4 %wt. The solution has been then stirred for several hours until it became homogeneous; this process was followed by 2 hours sonication to further improve the dispersion of the nanocellulose and promote its intimate contact with PVAm. The blended solution has been then poured in a Polystyrene petri dish with a diameter of 8.5 cm and dried overnight in a ventilated oven at 40 °C. Finally, the dried film was peeled off the petri dish and subjected to a thermal treatment in a vacuum oven at 105 °C for 2 hours. This was performed in order to remove any residual water, promote cellulose hornification and possibly favor the formation of amide bonds between MFC carbonyl groups and the polymer amine groups. The final thickness of the membranes resulted to be of about 45 µm with variation not exceeding 10 % for the different samples used for the tests.

3.2 Water sorption

The water uptake for the membranes was measured at 35 °C in the range 0-80 % humidity, using a quartz spring microbalance (Piccinini et al., 2004). In this apparatus, the sample is linked to a quartz spring placed in an evacuated, thermostatic, glass column. The sample weight is measured by monitoring the elongation of the spring upon water absorption. Tests were made by following a multiple steps procedure: the column is filled with a known pressure of water vapor and the penetrant uptake is measured by monitoring the spring displacement until the equilibrium conditions are reached; subsequently a further step is carried out by increasing the pressure of water vapor in the system. The equilibrium water uptake at the ith step is then calculated as shown in Eq(1).

$$[m_{water}]_i = (h_i - h_0) * k/g \tag{1}$$

Here k represents the spring elastic constant and h_i the spring length at i^{th} step, while h_0 is the initial spring length and g is the gravity acceleration; buoyancy force has been neglected in view of the low pressure at which the steps are carried out. Moreover, by analyzing the transitory phase during every single step, it has been also possible to estimate the Fickian diffusion coefficient, D, for the penetrant, through the following equation (Crank, 1979):

$$\frac{m_{sample}}{m_{sample,t\to\infty}} = 1 - \sum_n \frac{8}{(2n+1)^2\pi^2} exp\left[\frac{-D(2n+1)^2\pi^2 t}{L^2}\right] \tag{2}$$

where m_{sample} is the mass at time t, $m_{sample\to\infty}$ is the mass at the equilibrium condition and L is the sample thickness.

3.3 Gas Permeation

CO_2 and CH_4 permeability measurements in humid conditions have been investigated in a modified constant volume variable pressure setup, thoroughly described in a previous works (Catalano et al. 2012). The system is based on a closed-end downstream volume (V), in which the pressure (p_1) is constantly measured, whereas the feed pressure (p_2) is kept constant for the duration of the test. After a vacuum test ensures a good vacuum grade of the system, the gas permeability is calculated as shown in Eq(3).

$$P = -\left(\frac{dp_1}{dt}\right)_{t\to\infty} \frac{V}{RT}\frac{L}{A}\frac{1}{(p_1-p_2)} \tag{3}$$

L represents the sample thickness and A the permeation area. Before each test, the system is evacuated overnight in order to remove all chemical species from the membrane matrix. Subsequently, the membrane is equilibrated at a given water pressure, corresponding to the relative humidity (RH), at which the test will be carried out. Once the sample pre-equilibration is completed, a humidified gas stream, with the same water activity of the pre-equilibration step, is flown in the upstream side of the membrane. The pressure variation on the downstream side is then monitored until steady state conditions are obtained, allowing the permeability evaluation. Indeed, after an initial transient phase, related to the equilibration of the water across the membrane, the pressure variation is related only to the permeation of the incondensable species across the selective layer.

4. Results and Discussion

In Figure 1, the water sorption results for the MFC G2/PVAm blend after thermal treatment are showed. The absorbance of water has been measured at 35 °C with water activity ranging from 0.15 to 0.86 and the water uptake in the polymer increased from 0.016 g_{water}/g_{pol} to 0.52 g_{water}/g_{pol}. The shape of the sorption isotherm is the one usually observed for hydrophilic material, with a sudden variation in the slope of the curve, that is usually associated with the onset of the swelling of the polymeric matrix and the beginning of massive water clustering (Davis and Elabd, 2013). From the data collected, it can be seen how this swelling point occurs at a water intake slightly lower than 0.1 and at a water activity of about 0.6.

For the sake of comparison, Figure 1 also shows the absorption curves corresponding to pure MFC G2 (Minelli et al., 2010) and to a PVA/PVAm blend with a Polyvinylamine content of 80 % (Deng and Hagg, 2010). This last material have been subjected to a similar thermal treatment at 105 °C to induce cross-linking and can be considered to have water sorption more similar to that of PVAm than the currently investigated material.

It can be seen how the membrane prepared in this work is laying in between the two curves from literature. In particular, in the activity range from 0 to 0.5, the curves representing pure MFC and the 50-50 MFC/PVAm cured blend are substantially overlapping, while higher values of water absorption should be expected for the latter in view of higher PVAm water uptake with respect to MFC. This kind of behavior suggests that MFC fibers in the blends have lower solubility with respect to that of pure MFC. The thermal treatment thus appears to have successfully reduced the material sensitivity to water through the formation of new bonds between the cellulose fibers (hornification) or among amine groups of PVAm and the carboxylic ones on the surface of the

cellulose microfibrils (crosslinking). In particular, the fact that the water uptake appears to be simply delayed and not significantly decreased throughout the experiments suggests that the number of crosslinks, if any, is rather limited inside the matrix and that difference are more related to a densification of MFC network that prevent to some extent the water uptake of the more hydrophilic Lupamin domains. The overall behavior therefore can be described by considering that the MFC/PVAm films have a microstructure very similar to the one of pure nanocellulose, having PVAm as a secondary dispersed phase. Therefore, the MFC network acts as a constraint for PVAm and hinders its swelling until a critical RH is reached, where the fibrillar network breaks and the whole material rapidly swells due to water intake of Polyvinylamine.
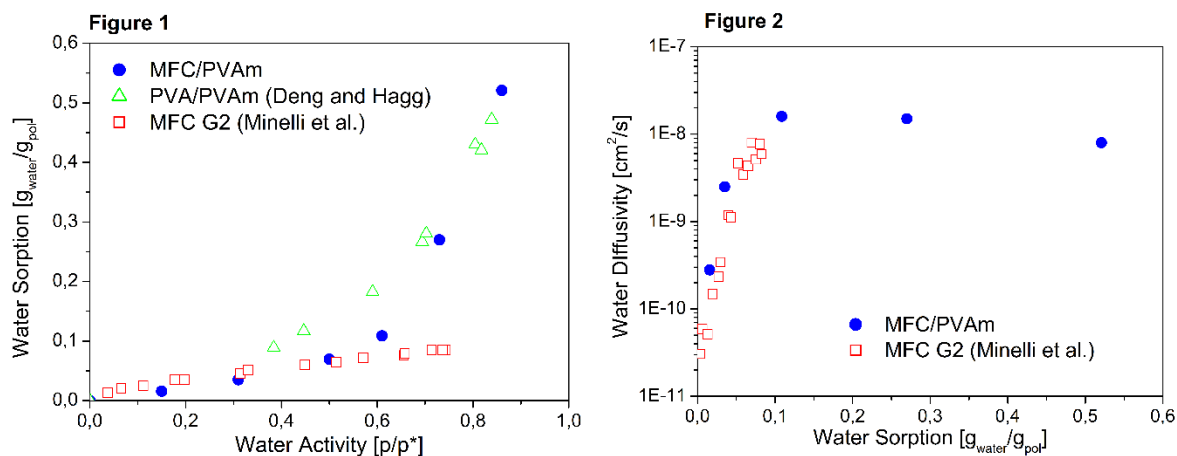

Figure 1 and 2: Water absorption curves as a function of water activity (left) and Fickian Diffusivity curves as a function of water intake (right) at 35°C for MFC/PVAm blend cured at 105°C (this work)(dots), pure carboxymethylated MFC G2 (Minelli et al., 2010) (squares), PVA(20 %)/PVAm(80 %) blend (Deng and Hagg, 2010)(triangles).

As mentioned above, sorption tests also allowed achieving information of the water diffusivity in the system.
The kinetic data were processed through Eq (2) and the results are reported in Figure 2, which shows the water diffusion coefficient plotted as a function of the water concentration inside the membrane. For uptakes up to 0.1 g_{water}/g_{pol} the sample developed in the present work (blue dots) shows a rapid increment of diffusivity, from 2.8E-10 to 1.6E-8 cm^2/s beyond this point however the diffusivity appears to hit a plateau, since no further significant increment can be observed. Again, for the sake of completeness, the water diffusivity values of a pure MFC G2 film have also been plotted (Minelli et al., 2010). As per the water sorption curve, the two curves present the same behavior up to the swelling point identified by a water intake of about 0.1 and actually reach the same plateau level at the higher concentration inspected.
Therefore, the addition of PVAm to the system does not appear to have an influence on the transport properties of the material at a low water concentration, confirming the similarity between the two material structures in the low activity range. PVAm indeed seems to allow simply a higher relaxation of the material, which therefore reaches a higher water uptake. In this concern it must be taken into account that the kinetic parameter showed in Figure 2 does not consider the relaxations processes sometime present during sorption, as it expresses only the Fickian contribution for the single sorption step.
On the other hand, the results of pure gas permeation tests are presented in Figure 3 for the different materials tested in the present work. A dramatic increase of different gas permeability, already seen in previous works for MFC based films (Minelli et al., 2010) is observed with a variation that in the present case is of about 3 orders of magnitude in the investigated humidity range (30-90 %). Throughout the whole humidity range, then, CO_2 appears to be the most permeable gas, showing a permeability up to two orders of magnitude higher than the one obtained for CH_4. For example, at 70 % relative humidity the CO_2 permeability in MFC/PVAm blends has a value of 89 Barrer against 0.8 Barrer for methane, while at 87 % relative humidity a value of 278 Barrer, the largest achieved in the present work, is observed that correspond to a methane permeability of about 10 Barrer. In the case of pure MFC films on the other hand CO_2 permeability ranges from around 10^{-2} Barrer at 10 % RH, up to 42 Barrer at 82 % RH while that of methane increases from 0.006 to 0,37 Barrer in the same water activity range thus remaining well below that of the other gas. These results can be explained considering that carbon dioxide is the gas with both the lowest kinetic diameter and the highest condensability (Baker and Lokhandwala, 2008) not to mention its high water solubility and, at least in case of MFC/PVAm, the possibility of interact with the fixed carriers present in the membrane.

As a comparison, Figure 3 presents also the permeability data taken from literature for a film of pure PVAm (Kim et al. 2013). It is notable how, for humidity values lower than the swelling point (60 % RH), CO_2 permeability of the MFC/PVAm blend is significantly lower than the one of pure PVAm, up to 2 orders of magnitude. This strengthens the idea that, at low humidity, these materials tends to be very similar to pure MFC to modify then their behavior as the RH increases. Indeed, at a higher water content, the swelling of the polymeric matrix induces in the material performances much closer to PVAm and in some cases even higher as present membranes reached a permeability values of about 255 Barrer at around 85 % RH, against the 130 Barrer obtained for the pure Polyvinylamine.

As a further confirmation of the observed behavior, it can be noticed that the CO_2 permeability of pure MFC assumes values very similar to those of the MFC/PVAm blend at humidites lower than 50 %, to then remain below that materials the high water activity range. Similar conclusions can be drawn also for the behavior of CH_4 permeability, as the MFC/PVAm blend and pure MFC curve tend to converge at low humidity and diverge at a higher one.
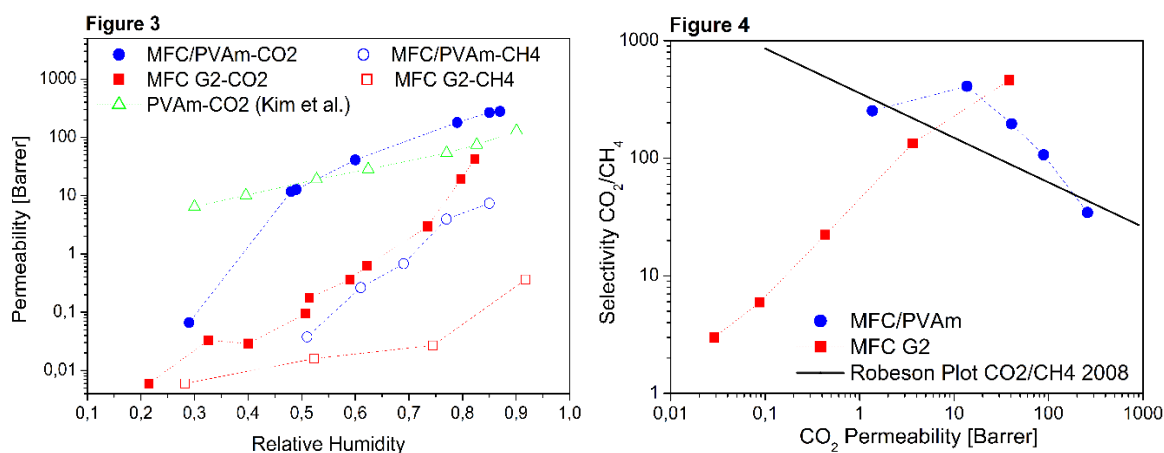

Figure 3 (left): Permeability of CO_2 and CH_4 for MFC/PVAm cured at 105 °C (dots), MFC G2 Pure (squares) (both from this work) and pure PVAm (Kim et al., 2013) (triangles) as a function of relative humidity.
Figure 4 (right): Selectivity of CO_2 over CH_4 as a function of CO_2 permeability for MFC/PVAm cured at 105 °C and pure MFC G2 (both from this work). Straight line represents Robeson upper limit at 2008 (evaluated for dry conditions).

Finally, Figure 4 shows the separation performance for both the MFC/PVAm blends and the pure MFC films in the CO_2/CH_4 Robeson Plot (Robeson, 2008). This plot represents the trade-off between permeability and selectivity typical of polymeric membranes and the black line represents the upper limit for the considered separation. Interestingly, the synthesized membranes are able to achieve attractive separation performances, especially in the intermediate humidity region, where the experimental data are well beyond the state-of-the-art of polymeric membranes: for example at a CO_2 permeability of 14 Barrer the cured membrane shows a selectivity up to 410 and remains above the line up to 70 % RH. Unfortunately, indeed, when the materials show a relevant increase of water uptake, which is at the highest activity inspected, the increase in permeability is accompanied by a substantial decrease in selectivity, which slowly bring the membranes below the trade-off curves of the 2008 Robeson's plot.

The good performance obtained by the MFC/PVAm blend, therefore, can be once again related to the reduced water uptake in the low activity region, which produces a matrix with limited swelling features, allowing the membrane to achieve superior separation performance. This conclusion is also confirmed by the fact that pure MFC films showed even higher selectivity than the blends (462 CO_2/CH_4 selectivity and 38.5 Barrer CO_2 permeability at 82 % RH) even if they cannot reach the same values of CO_2 permeability.

5. Conclusions

In the present work, a new type of membrane based on nanocellulose carboxymethylated fibers was prepared by blending them with polyvinylamine and treating the resulting material at high temperature in vacuum. This was done in order to improve the film stability at high humidity by decreasing water uptake and possibly creating covalent bonding through the fibers and the polymer. Sorption experiments allowed to confirm that thermal treatment was effective in limiting water uptake at least in the medium activity range where water

soprtion was indeed equalt to that of pure MFC films. The upturn of soprtion isotherm in the cured material indeed took place at about 60% RH reaching solubility values as high as 0.5 g/gpol.

This behavior allowed the material to maintain a low methane permeability for most of the medium activity range, which was then reflected by a selectivity as high as 410 at 50 % RH, paired with a CO_2 permeability of 13 Barrer, achieving separation performance well above the upper bound. Unfortunately, increasing water activity the difference between the two gas permeability reduces causing a strong decrease of selectivity when the relative humidity exceed 60 %.

In conclusion the present results shows that MFC ad MFC based membranes can be extremely interesting materials in the field of CO_2 separation, in particular if high selectivity is needed, however further investigations must be done, to increase the CO_2 permeability without losing selectivity, in order to make them suitable for real carbon capture applications.

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